The role of advection and dispersion in the rock matrix on the transport of leaking CO₂-saturated brine along a fractured zone

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Running Title: Reactive transport of CO₂-saturated brine along a fractured zone

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¹ COMSOL code is available upon request from the author.

Abstract: CO₂ that is injected into a storage reservoir can leak in dissolved form because of brine displacement from the reservoir, which is caused by large-scale groundwater motion. Simulations of the reactive transport of leaking CO_{2aq} along a conducting fracture in a clay-rich caprock are conducted to analyze the effect of various physical and geochemical processes. Whilst several modelling transport studies along rock fractures have considered diffusion as the only transport process in the surrounding rock matrix (diffusive transport), this study analyzes the combined role of advection and dispersion in the rock matrix in addition to diffusion (advection-dominated transport) on the migration of CO_{2aq} along a leakage pathway and its conversion in geochemical reactions. A sensitivity analysis is performed to quantify the effect of fluid velocity and dispersivity. Variations in the porosity and permeability of the medium are observed in response to calcite dissolution and precipitation along the leakage pathway. We observe that advection and dispersion in the rock matrix play a significant role in the overall transport process. For the parameters that were used in this study, advection-dominated transport increased the leakage of CO_{2aq} from the reservoir by nearly 205%, caused faster transport and increased the mass conversion of CO₂ in geochemical reactions along the transport pathway by approximately 12.20% compared to diffusive transport.

Keywords: Reactive transport, Advection dominated transport, Diffusive transport, CO₂-saturated brine leakage, Transport in fractures, Rock matrix, Calcite kinetic reaction

41 1. Introduction

42 CO₂ storage in geological formations is a method to slow the atmospheric
43 accumulation of greenhouse gases (Holloway, 2005; Middleton et al., 2012).
44 Environmental hazards that are related to geological CO₂ storage are associated with
45 its potential leakage from storage reservoirs (Stone et al., 2009; Haugan and Joos,
46 2004). The leakage risk is the greatest when the injected CO₂ remains as a supercritical
47 free-phase (CO₂) in the reservoir because of its lower density than the resident fluid (Pruess,
48 2006a, 2006b). However, the leakage risk diminishes with time because of the progressive
49 dissolution of supercritical CO₂ in the formation fluid (IPCC, 2005). Upon the complete
50 dissolution of CO₂ in the formation fluid (over 10,000 years), the leakage risk is only
51 associated with the dissolved phase (CO_{2aq}) (Bachu et al., 1994).

52 Recently, a relatively safer method of CO₂ geological sequestration has been
53 investigated, in which brine that carries CO_{2aq} is injected into the reservoir rather than
54 supercritical CO₂ (Aradóttir et al., 2012; Gislason and Oelkers, 2014). The downward

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55 movement of this brine that carries CO_{2aq} is expected because the injected fluid is
56 denser than the resident one. This mode of sequestration exhibits relatively faster and
57 higher consumption of CO_{2aq} through mineral trapping (Aradóttir et al., 2012).
58 However, large-scale groundwater motion may displace the brine from the reservoir,
59 creating an associated risk of CO_{2aq} leakage (Bachu et al., 1994; IPCC, 2005; Gaus,
60 2010).

61 The transport of CO_{2aq} may occur through a combination of processes, including advection,
62 dispersion, and diffusion (Bachu et al., 1994). In some cases, fractures or faults may serve as
63 the main leakage pathways (Grisak and Pickens, 2007). Leaking CO_{2aq} may undergo various
64 physical and geochemical interactions with the rock formation. Mass exchange between the
65 conducting fracture and the rock matrix, sorption, and geochemical reactions may immobilize

solute species in the fractured rocks (Neretnieks, 1980; Cvetkovic et al., 1999; Xu et al., 2001; Bodin et al., 2003). Low-pH brine that carries $\text{CO}_{2\text{aq}}$ may potentially undergo various geochemical reactions with its associated conversion through calcite dissolution or precipitation reactions (Dreybrodt et al., 1996; Kaufmann and Dreybrodt, 2007; Dreybrodt et al., 1997). Variations in the medium's porosity and permeability may result from mineral dissolution or precipitation because of geochemical interactions with leaking CO_2 -saturated brine. For example, the fast dissolution of carbonate minerals may widen the existing flow paths (Andreani et al., 2008; Gaus, 2010; Ellis et al., 2011(a, b)).

Gherardi et al. (2007) analyzed the geochemical interactions of leaking CO_2 and associated brine that carries $\text{CO}_{2\text{aq}}$ by means of numerical studies and reported porosity variations near the reservoir-caprock interface, which are mainly related to calcite mineral reactions. In an experimental study, Andreani et al. (2008) reported a 50% increase in the medium's porosity in close proximity of the fracture because of calcite dissolution from cyclic flows of CO_2 and CO_2 -saturated brine. Noiriél et al. (2007) examined the effects of acidic water in a flow-

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minerals in the fracture. Ellis et al. (2011a) performed a seven-day experiment to study the geochemical evolution of flow pathway in fractured carbonate caprock because of leaking $\text{CO}_{2\text{aq}}$ -carrying brine. These authors reported an increase in fracture apertures because of the preferential dissolution of calcite mineral. Ellis et al. (2011b) reported a flow-through experiment of acidic brine in fractured carbonate caprock (over 90% of the bulk rock composed of calcite and dolomite), which increased the fracture apertures close to the inlet boundary because of preferential calcite dissolution.

Peters et al. (2014) suggested including the complex geochemical interactions of CO_2 -saturated brine with mineral calcite in reactive transport models to investigate the permeability evolution of flow pathways in caprock. Nogues et al. (2013) suggested

disregarding minerals such as kaolinite, anorthite, and albite in geochemical models that involve the fate of CO₂-saturated water whenever carbonate minerals are abundant. Several authors conceptualized solute transport in a fracture-matrix system as a dual-domain model; transport in fractures occurs through advection, dispersion and diffusion, whereas diffusion alone is considered in the matrix (Steefel and Lichtner, 1998a, 1998b; Novak, 1993, 1996; Ahmad et al., 2015).

In this study, we consider the presence of an altered rock matrix zone (where advection and dispersion may not be negligible) that surrounds a fracture and how these processes affect the reactive transport of CO₂-saturated brine that is leaking along this fracture-matrix system. The velocity fields in the fracture and rock matrix are modelled by Brinkman equations while considering the time- and space-dependent variations in porosity and permeability that are caused by the dissolution and precipitation of calcite. Various transport scenarios are simulated for a period of 500 years to analyze the significance of adding advection and dispersion into the rock matrix compared to diffusion alone (diffusive transport) on the fate of

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leaking CO_{2aq} and its conversion in geochemical reactions along the leakage pathway. A comparative analysis between various reactive transport scenarios is presented in terms of variations in the medium's porosity, CO_{2aq} leakage fluxes from the reservoir, the retention of CO_{2aq} because of mass that is stored in aqueous and adsorbed states, and CO_{2aq} that is converted in geochemical reactions along the leakage pathway. A sensitivity analysis is also performed to determine the significance of the fluid velocity and dispersivity.

2. Model description

The formulation of the reactive transport problem involves a series of mass balance and momentum equations combined with constitutive thermodynamic relationships. The reactions that are considered in the study are displayed in Table 1. Reactions (R0)-

(R4) were considered to be fast and modelled as in equilibrium, whereas the calcite mineral reaction (R5) was considered a slow (kinetically controlled), reversible reaction. Reaction (R0) represents the equilibrium between supercritical CO₂ and CO_{2aq} and was only included in the batch geochemical models but excluded in the subsequent reactive transport modelling. The solubility of CO₂ in the fluid (reaction (R0)) was based on the relationships that were developed by Duan and Sun (2003) and later modified by Duan et al. (2006). This solubility model is valid for a wide range of pressures, temperatures, and ionic strengths. The equilibrium constants for remaining reactions (R1)-(R5) were obtained from the LLNL thermo database (Delany and Lundeen, 1990), the default thermodynamic database for The Geochemist's Workbench® (GWB), an integrated geochemical modelling package. Linear interpolation was used to compute the equilibrium constants of the reactions at the temperature that was used in the study. The activity coefficient of CO_{2aq} was computed from the model that was presented by Duan and Sun (2003). The B-dot model, an extension of the Debye-Hückel equation, was used to compute the activity coefficients of the involved aqueous species (Bethke, 2008).

Table 1. Chemical reactions that were considered for the CaCO₃-H₂O-CO₂ system.

No.	Reaction
(R0)	$\text{CO}_{2\text{g}} \leftrightarrow \text{CO}_{2\text{aq}}$
(R1)	$\text{H}_2\text{O} + \text{CO}_{2\text{aq}} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$
(R2)	$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$
(R3)	$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$
(R4)	$\text{Na}^+ + \text{HCO}_3^- \leftrightarrow \text{NaHCO}_{3\text{aq}}$
(R5)	$\text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-$

2.1. Model domain

Fig. 1 presents the schematic of a CO₂ storage reservoir that is overlain by a clay-rich caprock with a vertical conducting fracture. The domain involves a conducting fracture that is surrounded by a less-permeable rock matrix. W_f is the half-width of the fracture (taken as 1 mm), W_m is the half-width of the rock matrix (50 m), and L is the caprock length (100 m). The fracture is assumed to be partially filled with porous material (Wealthall et al., 2001; Wu et al., 2010; Laubach et al., 2010; Liu et al., 2013) and has an initial porosity of 0.60. The porosity of the rock matrix is taken as 0.12. The lower boundary of the caprock, and thus the upper boundary of the reservoir, is assumed to be at a depth of 1040 m below the land surface. The leaking CO₂-saturated brine from the reservoir enters the transport domain from the bottom inflow boundary, which comprises a fracture and rock matrix, and exits through the top (open) boundary. Continuity conditions for the solute and fluid mass are applied at the fracture-matrix interface. Symmetry with no-flow conditions are assumed at the left (center of the fracture) and right (center of rock matrix) boundaries.

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Figure 1. Schematic of the transport domain (clay-rich caprock with a vertical conducting fracture) that overlies the CO₂ storage reservoir.

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2.2. Reactive transport of aqueous species

The transport of aqueous species is defined by the following system of equations, which are written in terms of the chemical component species (COMSOL; Ahmad et al., 2015):

$$\mathbf{R}_f \theta \frac{\partial \mathbf{u}}{\partial t} + (1 - \mathbf{K}_d \rho_p) \mathbf{u} \frac{\partial \theta}{\partial t} - \nabla \cdot [(\mathbf{D}_D + \mathbf{D}_e) \nabla \mathbf{u}] + \nabla \cdot (\mathbf{v} \mathbf{u}) = \theta \mathbf{r}_{kin} \quad (1)$$

$$\mathbf{R}_f = 1 + \frac{\rho_{bulk}}{\theta} \mathbf{K}_d \quad (1b)$$

where $\mathbf{u}$ (x,y,t) is the vector of the concentration [mol/(kg water)] of the component species; $\mathbf{R}_f$ (x,y,t) is a diagonal matrix of the retardation factor, which considers sorption on the surface of the immobile mineral phases; $\mathbf{K}_d$ (x,y,t) is a diagonal matrix where the elements include the sorption partition coefficients of the component species

[m³/kg]; $\rho_{bulk} = (1 - \theta) \rho_p$ is the bulk density [kg/m³] of the porous media; θ (x,y,t) is the spatially and temporally varying porosity of the medium; ρ_p (x,y,t) is the particle density [kg/m³]; $\mathbf{D}_D$ is the dispersion tensor [m²/s]; $\mathbf{D}_e = \theta D_b \mathbf{I}$ is the effective

diffusion diagonal tensor [m²/s] with $\mathbf{I}$ as the identity tensor; D_b is the diffusion coefficient of CO_{2aq} in brine; $\mathbf{v}$ (x,y,t) is the specific flux [m/s], which is updated in

space and time; and $\mathbf{r}_{kin}$ (x,y,t) [mol/(s·kg water)] is the reaction term, which considers the consumption or production of component species from geochemical reactions ((R1)-(R5) in Table 1). The diffusion coefficient of CO_{2aq} in brine is computed at the pressure and temperature conditions that are used in this study from the relationships by Al-Rawajfeh (2004) and Hassanzadeh et al. (2008). The computed diffusion coefficient of CO_{2aq} in brine (3.05×10^{-9} m²/s) is considered for all the component species (Gherardi et al., 2007). The dispersion tensor in Eq. (1) is defined as a function of the dispersivity and the components of the fluid velocity by the following relationships (Bear, 1972):

$$\begin{cases} D_{Dxx} = \alpha_L \frac{v_x^2}{|v|} + \alpha_T \frac{v_y^2}{|v|} \\ D_{Dyy} = \alpha_L \frac{v_y^2}{|v|} + \alpha_T \frac{v_x^2}{|v|} \\ D_{Dxy} = D_{Dyx} = (\alpha_L - \alpha_T) \frac{v_x v_y}{|v|} \end{cases} \quad (2)$$

175 where α_L and α_T are the longitudinal and transverse dispersivity, respectively.

176 The transport Eq. (1) is written in terms of the component species ($\mathbf{u}$), which are linear
177 combinations of aqueous species that are unaffected by equilibrium reactions. The

178 methodology of Saaltink et al. (1998) allows us to express the mass conservation of
179 aqueous species and write the source/sink terms ($\mathbf{r}_{kin}$) in terms of the chemical
180 components. The concentration of aqueous species at every node in the computational

181 domain is then computed by solving the algebraic equations that relate the components
182 and aqueous species (speciation process, see Appendix A). In this study, eight aqueous
183 chemical species in the reaction system ((R1) to (R5) in Table 1) are transformed into

184 four component species. Therefore, $\mathbf{u}$ is a vector of size 4 and $\mathbf{R}_f$ and $\mathbf{K}_d$ are matrices
185 of size 4×4 . Eq. (1) is a system of nonlinear partial differential equations in which the

186 variables θ , ρ_p , and ρ_{bulk} , the matrices $\mathbf{R}_f$ and $\mathbf{K}_d$ and the vector $\mathbf{r}_{kin}$ are nonlinear
187 functions of the local concentration of the component species ($\mathbf{u}$).

188 2.3. Mass conservation of calcite mineral

189 The mass conservation of calcite mineral that undergoes kinetic reaction in the
190 transport domain (fracture and rock matrix) is modelled by using the following
191 ordinary differential equation (ODE):

$$192 \quad \frac{\partial c_{m,bulk}}{\partial t} = -\theta \rho_b r_m \quad (3)$$

where $c_{m,bulk}$ (x, y, t) is the concentration of mineral calcite per unit bulk volume [mol/m³], and the reaction term r_m (x, y, t) represents the consumption (dissolution) or production (precipitation) of calcite [mol/(s·kg water)]. The initial mineral concentration ($c_{m,bulk}$) values are computed to be 3142.03 and 6912.46 mol/m³ in the fracture and the rock matrix, respectively, based on the corresponding initial volume fraction of calcite (Table 2).

Table 2. Caprock mineralogical composition in the fracture and the rock matrix.

Mineral	Mineral volume fraction in unaltered rock (Gherardi et al., 2007)	Mineral volume fraction in the fracture for 0.60 porosity	Mineral volume fraction in the rock matrix for 0.12 porosity
Calcite	0.290	0.116	0.255
Dolomite	0.040	0.016	0.035
Quartz	0.200	0.080	0.176
Illite	0.020	0.008	0.018
K-feldspar	0	0	0
Chlorite	0.060	0.024	0.053
Albite	0	0	0
Kaolinite	0.050	0.020	0.044
Na-smectite	0.150	0.060	0.132
Muscovite	0.190	0.076	0.1672

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2.4. Mineral kinetic reaction

The mineral kinetic reaction (r_m) in Eq. (3) is defined in terms of the species concentration and mineral reactive surface area (Lasaga, 1994):

$$r_m = k_m A_m [1 - \Omega_m] \quad (4)$$

where k_m is the temperature-dependent kinetic rate constant of the mineral [mol/(s·m²)] and A_m is the reactive surface area of the mineral [m²/(kg water)], which is updated in time and space during the modeling process. The term $\Omega_m = Q_m/K_{eq}$ is the saturation state of calcite, where Q_m represents the calcite ion activity product, and K_{eq} is the equilibrium constant for

the mineral reaction. The mineral dissolves in the solution if the saturation state of the brine solution with respect to the mineral is less than unity and precipitates if $\Omega_m > 1$. The temperature dependence of the kinetic rate constant (k_m) of the mineral is described by the Arrhenius equation (Lasaga, 1984):

$$k_m = k_{25} \exp \left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] \quad (5)$$

where R ($= 8.314 \text{ J/(mol-K)}$) is the gas constant; T is the temperature [K]. E_a is the activation energy of calcite, and k_{25} is a reaction constant, which are set to 41.87 KJ/mol and $1.60 \times 10^{-9} \text{ mol/(s-m}^2\text{)}$, respectively, at 25°C (Svensson and Dreybrodt, 1992).

2.5. Mineral reactive surface area

The geometric approach is adopted to calculate the mineral reactive surface from the number of mineral grains (Johnson et al., 2004; Marini, 2007). The initial mineral reactive surface area (A_m) values are calculated to be 3.52 and $38.67 \text{ m}^2\text{/(kg water)}$ in the fracture and rock matrix, respectively, based on the initial volume fractions of calcite in Table 2. The mineral kinetic reaction causes variations in the number of mineral grains and, thus, in the reactive surface area. The following relationship models the variations in the reactive surface area of the mineral:

$$A_m = 0.1 \left(\frac{A_g}{\theta \rho_b V_g} \right) (MV c_{m,bulk}) \quad (6)$$

where A_g and V_g are the physical surface area and volume of a mineral grain, respectively (assumed to be spherical with a radius of $1.65 \times 10^{-5} \text{ m}$); MV is the molar volume of the mineral; and $c_{m,bulk}$ is the concentration of the mineral, which varies in time and space

because of the mineral kinetic reaction (3). The mineral reactive surface area is set to 10% of its computed physical surface area (Johnson et al., 2004).

2.6. Velocity field for the transport system

The velocity field in the fracture and rock matrix is defined by the Brinkman equations, where flow in porous media is described by a combination of the mass and momentum balances:

$$\frac{\partial(\theta\rho_b)}{\partial t} + \nabla \cdot (\rho_b \mathbf{v}) = 0 \quad (7)$$

$$\frac{\rho_b}{\theta} \left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \frac{\mathbf{v}}{\theta} \right] = -\nabla p + \nabla \cdot \left[\frac{\mu_b}{\theta} \left\{ (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) - \frac{2}{3} (\nabla \cdot \mathbf{v}) \mathbf{I} \right\} \right] - \left(\frac{\mu_b}{\kappa} \right) \mathbf{v} + \mathbf{F} \quad (8)$$

where ρ_b is the density [kg/m³] and μ_b is the dynamic viscosity [kg/(m-s)] of CO₂-saturated brine; p is the pressure [Pa]; and κ is the permeability of the porous medium [m²]. Gravity is included through the force term ($\mathbf{F} = -\rho_b \mathbf{g}$), where $\mathbf{g}$ is the gravitational acceleration vector [9.81 m/s²]. The brine density and viscosity are equal to 1000 kg/m³ and 6.27×10⁻⁴ kg/(m-s), respectively. The viscosity of the brine is computed from the model by Mao and Duan (2009) at 45°C and 105×10⁵ Pa (representing conditions at the lower boundary of the domain, which is assumed to be at a depth of 1040 m below the surface). The Brinkman equations expand Darcy's law by including an additional term that considers viscous transport in the momentum equation while treating both the pressure gradient and flow velocity as independent vectors. Popov et al. (2009) found that the Stokes-Brinkman equation can represent porous media that is coupled to free flow regions such as fractures, vugs, and caves, including material fill-in and suspended solid particles. The Brinkman equation is numerically attractive because it defines the flow field in two regions (free flow and porous media) by using only a single system of equations instead of a two-domain

253 approach (Gulbranson et al., 2010). The validity of the Brinkman equations in
 254 COMSOL for modelling flow in porous media has been reported in several works
 255 (e.g., Sajjadi et al., 2014; Chabonan et al., 2015; Golfier et al., 2015; Basirat et al.,
 256 2015).

257 2.7. Medium's porosity

258 The variations in the porosity of the porous medium from mineral dissolution and
 259 precipitation are modelled in time and space (in fracture and rock matrix) based on the
 260 updated volume fraction of the calcite mineral through the following relationship:

$$261 \quad \theta = 1 - VF_{rock,p} \quad (9)$$

262 where $VF_{rock,p} = \sum_m VF_{m,p}$ is the summation of the volume fractions of all the minerals
 263 forming the rock, and $VF_{m,p} = V_{m,p}/V_{rock,p}$ [-] represents the volume fraction (ratio of
 264 the mineral volume to the total bulk volume) of each mineral. Some numerical
 265 restrictions are applied (Xu et al., 2014): (i) the minimum threshold value of the
 266 mineral concentration is set to 1×10^{-7} mol/m³ to avoid the complete dissolution and
 267 corresponding disappearance of the mineral from the domain, and (ii) the minimum
 268 porosity of the medium is set to 1×10^{-3} to stop any further mineral precipitation below
 269 this value.

270 2.8. Medium's permeability

271 The medium's initial permeability is calculated by using the Kozeny-Carman relationship
 272 (e.g., Bear and Chang, 2010):

$$273 \quad \kappa_0 = C \frac{\theta_0^3}{(1-\theta_0)^2 (A_{rock,SSAV})^2} \quad (10)$$

where $A_{rock,SSAV}$ is the specific surface area of the solid rock per unit volume of the solid rock [m^2/m^3], which depends on the mineral composition of the porous media; C is a coefficient that equals 0.2; and θ_0 is the initial porosity of the medium. The initial estimated permeability values are $2.24 \times 10^{-10} \text{ m}^2$ in the conducting fracture and $3.71 \times 10^{-13} \text{ m}^2$ in the rock matrix according to the initial porosities of 0.60 and 0.12 and Eq. (10).

Mineral dissolution or precipitation changes the medium's porosity and permeability. The medium's permeability is updated in time and space by using the Kozeny-Carman relationship (Lai et al., 2014; Xu et al., 2014):

$$\kappa = \kappa_0 \frac{(1-\theta_0)^2 \theta^3}{(1-\theta)^2 \theta_0^3} \quad (11)$$

2.9. Sorption of mobile species

Different minerals have shown a capacity to adsorb CO_2 (Santschi and Rossi, 2006; Fujii et al., 2010; Tabrizy et al., 2013; Heller and Zoback, 2014). Santschi and Rossi (2006) reported that dissolved CO_2 adsorbs onto calcite mineral surfaces through the formation of an intermediate species $[\text{Ca}(\text{OH})(\text{HCO}_3)]$, with a partition coefficient of $6.6 \times 10^{-2} \text{ m}^3/\text{kg}$. In their experimental study, Fujii et al. (2010) observed the reversible nature of the sorption of CO_2 onto rocks and minerals at pressure and temperature conditions that are relevant to CO_2 geological storage. Heller and Zoback (2014) observed the lowest CO_2 adsorption capacity for “Eagle Ford 127” clay, which mainly consists of calcite (80%). From their study the values of partition coefficient were deduced as $7.39 \times 10^{-4} \text{ m}^3/\text{kg}$ and $3.33 \times 10^{-3} \text{ m}^3/\text{kg}$ for “Eagle Ford 127” and “Montney” clay types respectively at a pressure of $105 \times 10^5 \text{ Pa}$.

In this study a value of $2.50 \times 10^{-4} \text{ m}^3/\text{kg}$ was used as a partition coefficient that is lower than the values reported by Santschi and Rossi (2006) and by Heller and Zoback (2014). The

reason is that these authors used crushed rock in their experiments, whereas this study deals with intact rock, thus with smaller reactive surface areas. Additionally, we use the same partition coefficient for all the mobile species because of the large uncertainty in the sorption properties and complex geochemical interactions of all the species and to simplify the analysis.

2.10. Initial and boundary values

The initial pressure in the domain is defined as the hydrostatic pressure with a subsurface pressure gradient of 1×10^4 Pa/m (Pruess, 2008). The pressures equal 105×10^5 Pa at the bottom and 95×10^5 Pa at the top for this gradient and an atmospheric pressure of 1×10^5 Pa, assuming that the domain is located at a depth of 1040 m below the land surface. In the base-case transport scenarios, an excess pressure of 71.63 Pa in addition to the prevailing hydrostatic pressure is applied at the bottom boundary to obtain fluid Darcy velocities of 10 and 2×10^{-2} m/year in the conducting fracture and rock matrix, respectively. These velocities show a combined Darcy velocity of 0.0202 m/year for the fracture plus the matrix system. This velocity falls in the range for regional-scale Darcy velocities of 1 to 10 cm/year, which are measured in a number of sedimentary basins (Bachu et al., 1994).

The initial water chemistry in the reservoir and transport domain (clay-rich caprock) is obtained from the background Batch Geochemical Modelling (BGM). The background BGM is performed at a temperature of 45°C and CO₂ partial pressure of 1×10^3 Pa (Xu et al., 2005) and considers 0.5 M of NaCl solution until full equilibrium is reached (with respect to all the reactions in Table 1). The chemistry of the leaking CO₂-saturated brine is obtained from CO₂ dissolution modelling that is performed at a temperature of 45°C and CO₂ partial pressure of 105×10^5 Pa (representing a depth of 1040 m below the surface) for a 0.5 M NaCl solution.

Table 3 displays the initial water chemistry in the reservoir and clay-rich caprock (column 2) and that of the leaking CO₂-saturated brine in the reservoir (column 3). The compositions of the initial and boundary brines in the modelling process, written in terms of chemical components, are presented in Table 4. The composition of leaking brine at the bottom inflow boundary is set to remain constant during the entire simulation time, assuming that the brine in the reservoir always stays in equilibrium with calcite.

Table 3. Initial prevailing water chemistry in the reservoir and clay-rich caprock (column 2) and the chemistry of CO₂-saturated brine in the reservoir (column 3).

Pressure and temperature	45°C and 1×10 ³ Pa	45°C and 105×10 ⁵ Pa
Aqueous species	c [mol/(kg water)]	c [mol/(kg water)]
HCO ₃ ⁻	3.33×10 ⁻³	6.04×10 ⁻²
Na ⁺	4.99×10 ⁻¹	4.89×10 ⁻¹
Cl ⁻	5.00×10 ⁻¹	5.00×10 ⁻¹
Ca ²⁺	2.01×10 ⁻³	3.58×10 ⁻²
CO _{2aq}	1.98×10 ⁻⁴	1.08
H ⁺	5.44×10 ⁻⁸	1.67×10 ⁻⁵
OH ⁻	1.29×10 ⁻⁶	4.25×10 ⁻⁹
CO ₃ ²⁻	1.43×10 ⁻⁵	8.85×10 ⁻⁷
NaHCO _{3aq}	6.63×10 ⁻⁴	1.13×10 ⁻²
pH	7.26	4.78

Table 4. Initial (sub-index 0) and boundary conditions (sub-index bc) in terms of the chemical components. The translation of aqueous species to component species and viceversa can be seen in Appendix A.

Component species	Concentration [mol/(kg water)]	Component species	Concentration [mol/(kg water)]
u _{HCO₃,0}	4.02×10 ⁻³	u _{HCO₃,bc}	7.17×10 ⁻²
u _{Na0}	5.00×10 ⁻¹	u _{Na,bc}	5.00×10 ⁻¹
u _{Ca0}	2.01×10 ⁻³	u _{Ca,bc}	3.58×10 ⁻²
u _{CO₂,0}	1.82×10 ⁻⁴	u _{CO₂,bc}	1.08

2.11. Various reactive transport scenarios

Various reactive transport scenarios (Table 5) for leaking CO₂-saturated brine are performed to analyze the effects of different transport processes on the mobility and retention of CO_{2aq}, as well as the variations in the medium's porosity and permeability along the leakage pathway driven by geochemical reactions. The transport modelling of leaking CO₂-saturated brine is performed for a period of 500 years.

2.11.1. Base-case transport scenarios

We denote scenarios 1, 2, 3 and 4 as the base cases, aimed at investigating the roles of advection and dispersion in the rock matrix (advection-dominated transport) compared to diffusion alone (diffusive transport). In all cases, advection, diffusion and dispersion are considered to occur in the fracture. In scenarios 1 and 3, the mass transport in the rock matrix is modelled by considering that the only active transport process is diffusion, while scenarios 2 and 4 include advection and dispersion alongside diffusion in the rock matrix. Sorption is included in scenarios 3 and 4. The longitudinal and transverse dispersivity values for transport scenarios 1 and 3 are 10 m and 1 m, respectively, in the fracture and zero in the rock matrix. The same longitudinal and transverse dispersivity values are used in transport scenarios 2 and 4, but now both in the fracture and the rock matrix. The dispersivity values are related to the length scale of the transport domain, as reported by Gelhar et al. (1992).

Table 5. Various base-case reactive transport scenarios (1, 2, 3 and 4) and the reactive transport scenarios (5, 6, 7 and 8) in the sensitivity analysis.

Reactive transport scenario	Partition coefficient [m ³ /kg]	Initial velocity [m/year]	Longitudinal dispersivity in fracture / matrix [m]	Advection in the matrix	Excess pressure at the bottom [Pa]
1	0	10	10 / 0	N	71.625
2	0	10	10 / 10	Y	71.625
3	2.5×10^{-4}	10	10 / 0	N	71.625
4	2.5×10^{-4}	10	10 / 10	Y	71.625
5	0	5	10 / 10	Y	20.750
6	0	15	10 / 10	Y	122.50
7	0	10	20 / 20	Y	71.625
8	0	10	30 / 30	Y	71.625

2.11.2. Sensitivity analysis

Sensitivity analysis is performed to investigate the roles of fluid velocity and dispersivity on the reactive transport of CO_{2aq} along the leakage pathway. Thus, we perform additional reactive transport scenarios 5, 6, 7 and 8 (Table 5). Scenarios 5 and 6 involve, respectively, maximum fluid velocities of nearly 5 m/year and 15 m/year at the bottom (inlet) of the fracture, matching the regional-scale Darcy velocities that are characteristic of deep sedimentary basins (Bachu et al., 1994). These velocities are achieved by applying an excess pressure of 20.75 Pa and 122.50 Pa, respectively, in addition to the prevailing hydrostatic pressure at the bottom boundary. Pressures are kept constant in time, so that velocities vary in space and time driven by changes in porosity and permeability caused by mineral reaction. The longitudinal dispersivity values in scenarios 7 and 8 are 20 m and 30 m, respectively, in both the fracture and the rock matrix. A transverse dispersivity of 1 m is used in both the fracture and the rock matrix for transport scenarios 5 to 8 (sensitivity not tested).

2.12. Methodology of calculating the mass conversion of CO_{2aq} in geochemical reactions

The mass conversion of CO_{2aq} in geochemical reactions in each reactive transport scenario (Table 5) is calculated by comparing the mass balances with those from conservative transport scenarios (thus neglecting all the geochemical reactions in Table 1). The mass balance of CO_{2aq} in each scenario is calculated by considering the cumulative mass that enters the transport domain through the bottom inflow boundary, the mass that leaves through the top open boundary, and the mass that is stored in the aqueous and adsorbed states in the transport domain over time. The mass conversion of CO_{2aq} in geochemical reactions is presented in each reactive transport scenario as a percentage of the mass inflow as $\% m_{con} = \frac{m_{con}}{m_{in}} 100$, that is, the ratio between the cumulative mass conversion of CO_{2aq} in geochemical reactions (m_{con}) and its cumulative mass inflow (m_{in}) over time.

2.13. Numerical solution technique

The reactive transport coupled system of equations ((1)-(11)) with the corresponding initial and boundary conditions is modelled in COMSOL Multiphysics[®]. The flow and transport are modelled by adopting a one-domain approach with a single set of transport equations for the entire domain (fracture plus rock matrix) (Goyeau et al., 2003; Jamet et al., 2009; Tao et al., 2013; Basirat et al., 2015). In this study, we solve the non-linear system of equations that arises from coupled reactive transport modelling by using a segregated approach, which sequentially solves the various physics that are involved. Thus, the solution includes segregated solution steps with individual custom damping and tolerance. A damped version of Newton's method is used in all steps, with damping factors that equal unity. The flow problem (pressure and velocity field) is solved first (segregated step 1), the transport problem for

conservative species (components) is next (step 2), followed by the speciation problem (finding the aqueous species as a function of transport component species) in step 3; finally, the mass conservation equation of kinetic mineral calcite is solved in step 4. An implicit non-linear solver that is based on the backward differentiation formula (BDF) is used for time marching. The Jacobian matrix is updated every iteration to make the solver more stable. A structured mesh with quadrilateral elements is used as the numerical grid in the transport domain (fracture plus rock matrix). The mesh is refined in and near the fracture and towards the bottom inlet boundary (supplementary material). The complete mesh consists of 16560 quadrilateral elements. A total of 269509 degrees of freedom (DOF) are solved. The average time for solving each of the reactive transport scenarios is nearly 12 hours on an Intel(R) Core(TM)2 Quad CPU with RAM of 16 GB.

3. Results

The mixing of leaking CO₂-saturated brine with the resident pore waters in the transport domain (both the fracture and rock matrix in the clay-rich caprock) created a fluid under-saturated with respect to calcite, thus initiating calcite dissolution near the bottom inflow boundary. Calcite within the transport domain might dissolve or precipitate depending on the evolving geochemical conditions during the simulation.

3.1. Base-case reactive transport scenarios

The calcite dissolution and precipitation reactions, which are driven by leaking CO₂-saturated brine, caused variations in the medium's porosity and permeability in space and time along the transport pathway. Fig. 2a and 2b show the variations in the porosity and permeability in the rock matrix for the reactive transport scenario 2 after a simulation time of 500 years. The rock matrix's porosity increased by nearly 42% from

the initial value of 0.12 to a value of 0.17, whereas the permeability attained a value of $1.337 \times 10^{-12} \text{ m}^2$ from its initial value of $3.71 \times 10^{-13} \text{ m}^2$. This increase was mostly concentrated near the bottom inflow boundary because of continued calcite dissolution, which was driven by leaking CO_2 -saturated brine. A negligible decrease in porosity and permeability was observed towards the top of the transport domain along the conducting fracture, which indicates a small amount of calcite precipitation.

Figure 2. Variations in the porosity (a) and permeability (b) of the rock matrix in the base-case reactive transport scenario 2 after 500 years.

3.1.1. Role of advection and dispersion in the rock matrix

Figs. 3, 4 and 5 present the mass of $\text{CO}_{2\text{aq}}$ that entered the transport domain from the reservoir through the inflow boundary, its mass conversion in geochemical reactions and percent mass conversion, respectively, in the various studied reactive transport scenarios. In the advection-dominated transport scenarios 2 and 4, the combination of advection, dispersion and diffusion transport processes increased the leakage of $\text{CO}_{2\text{aq}}$ from the reservoir (Fig. 3a, 3b) and mass conversion during the geochemical reactions (Fig. 4a, 4b) along the transport domain compared to the corresponding values in diffusive transport scenarios 1 and 3.

441 The mass balances of $\text{CO}_{2\text{aq}}$ in the transport domain in the base-case reactive transport
442 scenarios 1, 2, 3 and 4 after 500 years are reported in Table 6. This table lists the $\text{CO}_{2\text{aq}}$ mass
443 inflows from the reservoir, the mass that was stored in aqueous and adsorbed states, the mass
444 that was converted in geochemical reactions, and the mass that left the transport domain
445 through the top open boundary.

Figure 3. Mass inflow of $\text{CO}_{2\text{aq}}$ through the bottom inflow boundary in various reactive transport scenarios over time: (a) scenarios 1 and 2; (b) scenarios 3 and 4; (c) scenarios 1 and 3; (d) scenarios 2 and 4; (e) scenarios 2, 5 and 6; and (f) scenarios 2, 7 and 8.

Figure 4. Mass conversion of $\text{CO}_{2\text{aq}}$ in various reactive transport scenarios over time: (a) scenarios 1 and 2; (b) scenarios 3 and 4; (c) scenarios 1 and 3; (d) scenarios 2 and 4; (e) scenarios 2, 5 and 6; and (f) scenarios 2, 7 and 8.

Figure 5. Percentage mass conversion of $\text{CO}_{2\text{aq}}$ in various reactive transport scenarios over time; (a) scenarios 1 and 2; (b) scenarios 3 and 4; (c) scenarios 1 and 3; (d) scenarios 2 and 4; (e) scenarios 2, 5 and 6; and (f) scenarios 2, 7 and 8.

The total mass inflow was split in terms of advective, dispersive and diffusive fluxes through the bottom inflow boundary both at the fracture and in the rock matrix. The highest mass inflow, mass that was stored in an aqueous state and mass conversion of $\text{CO}_{2\text{aq}}$ were associated with the advection-dominated transport scenarios 2 and 4 compared to the values in the corresponding diffusive transport scenarios 1 and 3. Higher stored mass in an adsorbed state can also be observed in the advection-dominated transport scenario 4 compared to the corresponding diffusive transport scenario 3. The mass balance errors were less than 0.1% in all the scenarios.

Table 6. $\text{CO}_{2\text{aq}}$ mass balance [mol] in the base-case reactive transport scenarios 1, 2, 3, and 4 after 500 years.

Reactive transport scenarios	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Total mass that entered the domain	5.98×10^4	5.26×10^5	1.39×10^5	5.62×10^5
Mass that entered from advection (fracture)	5.70×10^3	5.56×10^3	6.04×10^3	5.78×10^3
Mass that entered from diffusion (fracture)	1.79×10^0	2.94×10^{-1}	3.85×10^0	1.68×10^0
Mass that entered from dispersion (fracture)	3.19×10^3	5.12×10^2	7.21×10^3	3.02×10^3
Mass that entered from advection (matrix)	0	5.12×10^5	0	5.12×10^5
Mass that entered from diffusion (matrix)	5.09×10^4	4.86×10^3	1.26×10^5	2.49×10^4
Mass that entered from dispersion (matrix)	0	3.12×10^3	0	1.60×10^4
Mass that left the domain (fracture)	9.24×10^{-1}	1.69×10^2	9.14×10^{-1}	9.14×10^{-1}
Mass that left the domain (matrix)	0.00×10^0	3.32×10^3	0.00×10^0	8.65×10^1
Mass stored in an aqueous state	5.59×10^4	5.19×10^5	2.22×10^4	9.31×10^4
Mass stored in an adsorbed state	0.00×10^0	0.00×10^0	1.09×10^5	4.60×10^5
Mass converted in the geochemical reactions	3.86×10^3	4.09×10^3	7.57×10^3	8.49×10^3
Mass conversion of $\text{CO}_{2\text{aq}}$ after 500 years (%)	6.46×10^0	7.79×10^{-1}	5.45×10^0	1.51×10^0
Error in the mass balance (%)	1.82×10^{-2}	-9.16×10^{-2}	1.97×10^{-2}	1.34×10^{-2}

The mass balance for mineral calcite and Ca^{2+} and the split for the mass of calcite [mol] and pore volume [m^3] in the fracture and rock matrix in the base-case transport scenarios 1, 2, 3 and 4 after 500 years are presented in Table 7. Calcite dissolution prevailed over precipitation in the transport domain during the simulations, which implies a decrease in its mass and increase in the overall pore volume in the fracture and rock matrix. Considering advection in the rock matrix (scenarios 2 and 4) increased the calcite dissolution, pore volume and mass of Ca^{2+} compared to the corresponding diffusive transport scenarios 1 and 3. Moreover, relatively higher calcite dissolution occurred in the fracture than in the rock matrix compared to the initial mass of calcite in the fracture and rock matrix because of the higher advective velocity in the former. Finally, the mass of produced Ca^{2+} was equal to the mass of dissolved calcite (except for the mass balance errors of less than 0.14%).

Table 7. Mass balance [mol] of calcite and Ca^{2+} and increase in the pore volume [m^3] in the transport domain for the base-case reactive transport scenarios (1, 2, 3, and 4) after 500 years.

Reactive transport scenarios	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Mass of dissolved calcite in the fracture	7.26×10^0	7.33×10^0	1.24×10^1	1.36×10^1
Decrease in mass in the fracture (%)	2.31×10^0	2.33×10^0	3.94×10^0	4.33×10^0
Mass of dissolved calcite in the rock matrix	3.81×10^3	4.07×10^3	7.58×10^3	8.36×10^3
Decrease in mass in the rock matrix (%)	1.10×10^{-2}	1.18×10^{-2}	2.19×10^{-2}	2.42×10^{-2}
Total mass of dissolved calcite	3.81×10^3	4.08×10^3	7.59×10^3	8.38×10^3
Increase in pore volume in the fracture	2.68×10^{-4}	2.71×10^{-4}	4.57×10^{-4}	5.02×10^{-4}
Increase in pore volume in the rock matrix	1.41×10^{-1}	1.50×10^{-1}	2.80×10^{-1}	3.09×10^{-1}
Total increase in the pore volume	1.41×10^{-1}	1.51×10^{-1}	2.80×10^{-1}	3.09×10^{-1}
Mass of produced Ca^{2+}	3.81×10^3	4.08×10^3	7.58×10^3	8.37×10^3
Error in the mass balance (%)	-1.03×10^{-1}	-4.75×10^{-2}	1.42×10^{-1}	4.40×10^{-2}

Sorption in the transport scenarios 3 and 4 increased the $\text{CO}_{2\text{aq}}$ leakage from the reservoir (Fig. 3c, 3d) and mass conversion of $\text{CO}_{2\text{aq}}$ in the geochemical reactions (Fig. 4c, 4d) in the transport domain compared to the transport scenarios 1 and 2, which did not consider sorption. Comparing the sorption scenario-3 with the corresponding no-sorption scenario 1 and the sorption scenario 4 with the no-sorption scenario 2 indicates that sorption almost

doubled the mass conversion of $\text{CO}_{2\text{aq}}$ in the geochemical reactions (row 13 of Table 6); calcite dissolution (row 6 of Table 7), with an associated increase in pore volume (row 9 of Table 7); and production of Ca^{2+} (row 10 of Table 7).

Although the advection-dominated transport scenarios 2 and 4 increased the conversion of $\text{CO}_{2\text{aq}}$ mass [mol] in the geochemical reactions compared to the corresponding diffusive transport scenarios 1 and 3, decreasing trends in the percentage mass conversion were observed (Fig. 4a vs Fig. 5a and Fig. 4b vs Fig. 5b). Similarly, higher $\text{CO}_{2\text{aq}}$ mass conversion occurred in the sorption transport scenarios 3 and 4 compared to the corresponding no-sorption transport scenarios 1 and 2, yet decreasing trends were observed for the percent mass conversion in these scenarios (Fig. 4c vs Fig. 5c and Fig. 4d vs Fig. 5d). This result can be explained by the variability in the $\text{CO}_{2\text{aq}}$ mass inflows.

3.2. Sensitivity analysis

3.2.1. Role of velocity magnitude

Different initial fluid velocities prevailed in the fracture and rock matrix because of different excess pressure at the bottom boundary of the transport domain in scenarios 2, 5, and 6; velocities then changed during the simulation time due to variations in porosity and permeability. Mass inflows (Fig. 3e) and $\text{CO}_{2\text{aq}}$ mass conversion in the reactions (Fig. 4e) increased with the initial fluid velocity in the transport pathway. However, the percentage of mass conversion of $\text{CO}_{2\text{aq}}$ decreased with increasing fluid velocity (Fig. 5e). The mass conservation indicated that the mass inflow and mass conversion of $\text{CO}_{2\text{aq}}$ in the geochemical reactions increased with increasing fluid velocity in the transport domain (Table 6 and 8). Additionally, the mass of dissolved calcite, the pore volume and the mass production of Ca^{2+} increased with increasing fluid velocity in scenarios 2, 5 and 6.

Table 8. CO_{2aq} mass balance [mol] for the different reactive transport scenarios 5, 6, 7, and 8 after 500 years.

Reactive transport scenarios	Scenario 5	Scenario 6	Scenario 7	Scenario 8
Total mass that entered the domain	2.69×10^5	7.85×10^5	5.29×10^5	5.33×10^5
Mass that entered from advection (fracture)	2.77×10^3	8.31×10^3	5.60×10^3	5.61×10^3
Mass that entered from diffusion (fracture)	6.23×10^{-1}	1.89×10^{-1}	3.14×10^{-1}	3.24×10^{-1}
Mass that entered from dispersion (fracture)	5.42×10^2	4.95×10^2	1.10×10^3	1.70×10^3
Mass that entered from advection (matrix)	2.55×10^5	7.68×10^5	5.12×10^5	5.12×10^5
Mass that entered from diffusion (matrix)	9.03×10^3	3.38×10^3	4.75×10^3	4.68×10^3
Mass that entered from dispersion (matrix)	1.45×10^3	4.85×10^3	6.11×10^3	9.04×10^3
Mass that left the domain (fracture)	4.74×10^{-1}	2.03×10^3	2.92×10^2	4.03×10^2
Mass that left the domain (matrix)	4.32×10^1	1.35×10^5	6.26×10^3	9.40×10^3
Mass stored in an aqueous state	2.66×10^5	6.42×10^5	5.18×10^5	5.18×10^5
Mass stored in an adsorbed state	0	0	0	0
Mass converted in the geochemical reactions	3.50×10^3	4.42×10^3	4.81×10^3	5.43×10^3
Mass conversion of CO _{2aq} after 500 years (%)	1.30×10^0	5.63×10^{-1}	9.10×10^{-1}	1.02×10^0
Error in the mass balance (%)	5.47×10^{-3}	4.83×10^{-2}	-1.01×10^{-1}	-1.03×10^{-1}

Table 9. Mass balance [mol] of calcite and Ca²⁺ and increase in the pore volume [m³] in the transport domain for the different transport scenarios 5, 6, 7, and 8 after 500 years.

Reactive transport scenarios	Scenario 5	Scenario 6	Scenario 7	Scenario 8
Mass of dissolved calcite in the fracture	4.65×10^0	4.88×10^0	7.43×10^0	8.54×10^0
Decrease in mass in the fracture (%)	1.48×10^0	1.55×10^0	2.36×10^0	2.72×10^0
Mass of dissolved calcite in the rock matrix	3.48×10^3	4.43×10^3	4.80×10^3	5.40×10^3
Decrease in mass in the rock zone	1.01×10^{-2}	1.28×10^{-2}	1.39×10^{-2}	1.56×10^{-2}
Total mass of dissolved calcite	3.49×10^3	4.43×10^3	4.80×10^3	5.41×10^3
Increase in pore volume in the fracture	1.72×10^{-4}	1.80×10^{-4}	2.74×10^{-4}	3.15×10^{-4}
Increase in pore volume in the rock matrix	1.29×10^{-1}	1.63×10^{-1}	1.77×10^{-1}	1.99×10^{-1}
Total increase in the pore volume	1.29×10^{-1}	1.64×10^{-1}	1.77×10^{-1}	2.00×10^{-1}
Mass of produced Ca ²⁺	3.49×10^3	4.43×10^3	4.81×10^3	5.41×10^3
Error in the mass balance (%)	6.16×10^{-3}	5.32×10^{-2}	-1.07×10^{-1}	-1.13×10^{-1}

3.2.2. Role of longitudinal dispersivity

The higher longitudinal dispersivity very slightly increased the mass inflow (5.26×10^5 , 5.29×10^5 and 5.33×10^5 mol in scenarios 2, 7 and 8, respectively) (Figs. 3f and 4f; Tables 6 and 8). However, the mass conversion of $\text{CO}_{2\text{aq}}$ in the geochemical reactions (Fig. 4f) and percent mass conversion (Fig. 5f) increased with increasing dispersivity. In these scenarios, the higher quantities of $\text{CO}_{2\text{aq}}$ that were converted in the geochemical reactions for almost the same mass inflows resulted in similar trends for $\text{CO}_{2\text{aq}}$ mass conversion and its percentage of mass conversion (Figs. 4f and 5f; Table 8). For a given fluid velocity, the mass of dissolved calcite, the mass of produced Ca^{2+} , and the pore volume increased with the longitudinal dispersivity (Tables 7 and 9).

3.3. Breakthrough curves of leaking $\text{CO}_{2\text{aq}}$

The effects of advection and dispersion in the rock matrix on the transport of leaking $\text{CO}_{2\text{aq}}$ are presented in the form of breakthrough curves, which represent its concentration at 10 and 20 m locations from the bottom inlet boundary along the conducting fracture over time (Fig. 6). Fast migration of $\text{CO}_{2\text{aq}}$ along the leakage pathway was observed in the advection-dominated transport scenarios compared to the diffusive transport scenarios. Fast transport that was mainly driven by advection increased the $\text{CO}_{2\text{aq}}$ concentration in the advection-dominated transport scenario 2 compared to the diffusive transport scenario 1 after a travel distance of 10 and 20 m along the conducting fracture. Additionally, the highest velocity in scenario 6 resulted in the highest concentration of $\text{CO}_{2\text{aq}}$ (Fig. 6a and 6c). During earlier times, the higher dispersivity in scenario 8 increased the concentration of $\text{CO}_{2\text{aq}}$ (Fig. 6b and 6d). However, the lowest dispersivity value used in scenario 2 resulted in the highest $\text{CO}_{2\text{aq}}$ concentration after 67 and 135 years for the 10- and 20-m locations, respectively. This result

occurred because of the fast spreading and dilution of species concentration that was caused by higher dispersion along the transport pathway over time in scenario 8.

Figure 6. Breakthrough curves for $\text{CO}_{2\text{aq}}$ for various reactive transport scenarios at various locations along the fracture over time; (a) scenarios 1, 2, 5, and 6 at 10 m from the inflow boundary; (b) scenarios 1, 2, 7, and 8 at 10 m; (c) scenarios 1, 2, 5, and 6 at 20 m from the inflow boundary; and (d) scenarios 1, 2, 7, and 8 at 20 m.

4. Discussion

The role of calcite kinetics in contact with CO_2 -saturated brine in the reservoir in the presence of free-phase CO_2 in the reservoir has been investigated. For the purpose, two sets of CO_2 dissolution modelling have been performed for elevated values of $\text{CO}_{2\text{aq}}$ in the presence of free-phase CO_2 in the reservoir for calcite was (i) reactive and (ii) non-reactive. The presence

of calcite kinetics provided buffer and kept pH at a higher value of 4.78 whereas pH settled at 3.56 in the absence of calcite reaction. This added alkalinity caused by calcite dissolution may shift $\text{CO}_{2\text{aq}}$ into other ions in solution along the transport domain. Calcite dissolution in the reactive transport scenarios mainly occurred in close vicinity to the bottom inflow boundary (Gherardi et al., 2007; Andreani et al., 2008; Ellis et al., 2011b), resulting in the simultaneous production of Ca^{2+} and HCO_3^- , which brought the brine solution closer to calcite saturation away from the inflow boundary. The resulting saturation conditions with respect to calcite stopped any significant calcite dissolution in the rock matrix beyond 0.1 m from the inflow boundary, and caused mineral precipitation towards the top of the transport domain, mainly close to the conducting fracture. However, calcite precipitation was too low to have any significant effect on the decrease in porosity and permeability in the fracture and rock matrix.

In scenario 6, the rock matrix's porosity attained a value of 0.17 after 500 years at the inflow boundary but reached a value of 0.15 (the initial one was 0.12) approximately 0.01 m from the boundary. However, the rock matrix's porosity close to the fracture was higher than 0.15 up to a distance of 0.25 m from the inflow boundary in scenario 6. This result can be explained by the fast transport along the fracture, which caused calcite dissolution to occur over a relatively longer distance.

Declining trends in the percent mass conversion after some initial times that were observed in Fig. 5d as compared to Fig. 5c, are related to additional advection in the rock matrix in the advection-dominated transport scenarios 2 and 4. The percent mass conversion in scenarios 2 and 4 fell off after 2.01×10^6 s and 1.89×10^7 s, respectively (Fig. 5a, 5b, and 5d) but continued to increase in scenarios 1 and 3 (Fig. 5a, 5b, and 5c). Advection in scenarios 2 and 4 increased the mass inflows at an almost constant rate, whereas the mass inflow decreased with time in scenarios 1 and 3 due to the decreasing diffusive fluxes across the inflow boundary. Although the concentration gradients across the inflow boundary kept decreasing over time in all these

transport scenarios, the diffusive fluxes were the only transport process across the inflow boundary in the diffusive transport scenarios 1 and 3, which decreased the mass inflow compared to the corresponding inflows in the advection-dominated transport scenarios 2 and 4. Thus, the higher mass inflow in scenarios 2 and 4 with time created declining trends in percent mass conversion (Fig. 5a, 5b, and 5d).

The higher observed mass conversion of $\text{CO}_{2\text{aq}}$ in the geochemical reactions in sorption scenarios 3 and 4 compared to the corresponding no-sorption scenarios 1 and 2 (Fig. 4c and 4d) were mainly related to (i) the higher mass inflows through the inflow boundary induced by sorption and, to a lesser extent, (ii) the lower saturation state of calcite in the transport domain when sorption was included in the simulations. Over time, relatively lower saturation of calcite (mineral) prevailed in the transport domain in the sorption scenarios 3 and 4 compared to the no-sorption scenarios 1 and 2. The sorption process fixed the mass of Ca^{2+} and HCO_3^- onto the rock surfaces and lowered the concentration of these species in an aqueous state. This process lowered the saturation state of calcite in the sorption scenarios 3 and 4, promoting calcite dissolution and thus contributing towards the overall higher $\text{CO}_{2\text{aq}}$ mass conversion in the geochemical reactions in these scenarios.

Higher percent mass conversion occurred during earlier times in the no-sorption scenarios 1 and 2 compared to the corresponding sorption scenarios 3 and 4 (Fig. 5c and 5d). This result mainly occurred because sorption (scenarios 3 and 4) induced relatively higher concentration gradients across the inflow boundary; thus, higher diffusive fluxes resulted in higher mass inflows. Sorption fixed the species' masses in an adsorbed state and reduced their concentrations in an aqueous state, increasing the concentration gradients and mass inflows and decreasing the percent mass conversion during these earlier times.

This study shows that pH distribution along the transport pathway alone cannot fully predict the calcite reaction kinetics and the related conversion of $\text{CO}_{2\text{aq}}$ into other ions; instead the reactive process is mostly controlled by the saturation state of calcite. As an example, at a pH of 7.26, the brine was at saturation with respect to calcite and thus no reaction occurred in the transport domain before leakage of CO_2 -saturated brine started taking place. On the other hand, leaking CO_2 -saturated brine was at a pH of 4.78, and also saturated with respect to calcite, so again no reaction was driven. It was only the mixing of the two fluids (one prevailing in the transport pathway and the other one leaking from the reservoir) that brought the saturation state of calcite below one and caused calcite dissolution, concentrated initially in the vicinity of the lower leaking boundary. Over time, the calcite reaction zone advanced in the transport domain; however, due to the increase in Ca^{+2} and HCO_3^- as a result of calcite dissolution, the saturation state started increasing away from the lower leaking boundary. Eventually geochemical conditions evolved when saturation state with respect to calcite reached one; as a consequence, calcite dissolution ceased even though the pH value was 4.78 (representing leaking CO_2 -saturated brine), much lower than the initial value of 7.26 prevailing in the transport pathway. This shows that the fall in the pH value along the transport pathway did not fully predict the calcite reaction regimes; instead calcite reactivity and related conversion of $\text{CO}_{2\text{aq}}$ was found related to saturation state of calcite in the transport domain for the modelled leakage scenarios.

We computed the saturation state of calcite in the full domain (fracture plus rock matrix) in the no-sorption scenarios 1 and 2 and the corresponding sorption scenarios 3 and 4 over a simulation time of 500 years to further illustrate the role of sorption in maintaining a relatively lower saturation state of calcite, inducing dissolution. The saturation state of calcite was computed as its integral over the entire domain and simulation time. Fig. 7 presents the difference of the saturation state of calcite between the sorption scenarios and the

corresponding no-sorption scenarios. Except for the very early times (2.34×10^{-3} year), the saturation state of calcite remained lower in the sorption scenarios 3 and 4 compared to the corresponding no-sorption scenarios 1 and 2. The resulting low saturation state of calcite from sorption increased the conversion of CO_2 through the higher dissolution of calcite.

Figure 7. Difference of the saturation state of calcite (Ω_m) in the transport domain over time: between the sorption scenario 3 and the corresponding no-sorption scenario 1; and between the sorption scenario 4 and the corresponding no-sorption scenario 2.

The steep observed gradients of the percent mass conversion of $\text{CO}_{2\text{aq}}$ during the early times in all the reactive transport scenarios are related to the prevailing higher calcite dissolution reaction rate and associated higher mass conversion of $\text{CO}_{2\text{aq}}$ relative to the mass inflow through the bottom inflow boundary. During the earlier times, leaking CO_2 -saturated brine induced the lowest saturation of calcite and, thus, the highest calcite dissolution reaction rate and $\text{CO}_{2\text{aq}}$ mass conversion. Furthermore, the mass conversion of $\text{CO}_{2\text{aq}}$ in the geochemical reactions for all the reactive transport scenarios was well correlated with the calcite dissolution and associated increase in pore volume in the transport domain over time (Fig. 4 vs Fig. 8).

Figure 8. Increase in pore volume within the transport domain from calcite dissolution in various reactive transport scenarios over time: (a) scenarios 1 and 2; (b) scenarios 3 and 4; (c) scenarios 1 and 3; (d) scenarios 2 and 4; (e) scenarios 2, 5 and 6; and (f) scenarios 2, 7 and 8.

For the same initial fluid velocity at the bottom boundary of the fracture, the highest $\text{CO}_{2\text{aq}}$ concentration along the fracture in the advection-dominated transport scenario 2 indicates lower mass transfer from the conducting fracture into the rock matrix, when compared to that in the diffusive transport scenario 1 (Fig. 6a, 6b). The fast transport of $\text{CO}_{2\text{aq}}$ from advection in the rock matrix in the advection-dominated transport scenario 2 created low concentration gradients across the fracture-matrix interface that, in turn, decreased the diffusive mass transfer from the conducting fracture into the rock matrix.

5. Conclusions

This work presents the results of reactive transport simulations of CO_2 -saturated brine that leaks along a conducting fracture and a surrounding rock matrix in clay-rich caprock. The model that was developed here considered the effects of advection, dispersion and diffusion in both the fracture and rock matrix on the quantities of leaked $\text{CO}_{2\text{aq}}$, the evolution of the medium's porosity and permeability because of geochemical reactions, and the conversion of $\text{CO}_{2\text{aq}}$ in geochemical reactions along the leakage pathway.

Advection and dispersion in addition to diffusion in the rock matrix increased the leakage of $\text{CO}_{2\text{aq}}$ from the reservoir and its transport speed along the leakage pathway (arriving faster and further) as compared to the scenarios where transport occurred only by diffusion in the rock matrix. The amount of $\text{CO}_{2\text{aq}}$ that leaked from the reservoir was also found to increase with fluid velocity along the leakage pathway. The mass conversion of $\text{CO}_{2\text{aq}}$ in the geochemical reactions was found to increase with the fluid velocity and dispersion for the same set of hydraulic and geochemical parameters. The observed increase in $\text{CO}_{2\text{aq}}$ leakage from the reservoir and the amount that was consumed in the geochemical reactions implies that advection and dispersion in the

rock matrix are important transport processes that must be considered in addition to diffusion when modelling the leakage of $\text{CO}_{2\text{aq}}$ along a fractured pathway.

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APPENDIX

Appendix A: Writing the chemical component species from the aqueous species involved in the equilibrium and mineral kinetic reactions for the reactive transport system

A total of eight aqueous species (HCO_3^- , Na^+ , $\text{CO}_{2\text{aq}}$, Ca^{2+} , H^+ , OH^- , CO_3^{2-} , and $\text{NaHCO}_{3\text{aq}}$) are involved in four of the equilibrium reactions (R1) to (R4) and the mineral kinetic reaction (R5), which are presented in Table 1. Following the formulation by Saaltink et al. (1998), these eight aqueous species can be converted into four chemical components and written in

vector form: $\mathbf{u}^T = (u_{\text{HCO}_3}, u_{\text{Na}}, u_{\text{CO}_2}, u_{\text{Ca}})^T$, with the components defined as

$$\begin{cases} u_{\text{HCO}_3} = c_{\text{HCO}_3^-} - c_{\text{H}^+} + c_{\text{OH}^-} + 2c_{\text{CO}_3^{2-}} + c_{\text{NaHCO}_{3\text{aq}}} \\ u_{\text{Na}} = c_{\text{Na}^+} + c_{\text{NaHCO}_{3\text{aq}}} \\ u_{\text{CO}_2} = c_{\text{CO}_{2\text{aq}}} + c_{\text{H}^+} - c_{\text{OH}^-} - c_{\text{CO}_3^{2-}} \\ u_{\text{Ca}} = c_{\text{Ca}^{2+}} \end{cases} \quad (\text{A.1})$$

By transforming all the aqueous species in the reactions into the component species, the required number of transport equations decreases to four (number of chemical component species) from the original eight (number of aqueous species). The source/sink term in transport equation (1) takes the following form:

$$\mathbf{r}_{\text{kin}} = \begin{cases} r_{u\text{HCO}_3} = 2r_m \\ r_{u\text{Na}} = 0 \\ r_{u\text{CO}_2} = -r_m \\ r_{u\text{Ca}} = r_m \end{cases} \quad (\text{A.2})$$

Thus, the source/sink term ($\mathbf{r}_{\text{kin}}$) provides information regarding the changes in the chemical component species that are driven by the combined effects of equilibrium and mineral kinetic reactions in the reactive transport equation (1). The term (r_m) represents the kinetic reaction (dissolution or precipitation) of mineral calcite, which was defined in equation (4). From (A.2) it is immediately seen that $\mathbf{r}_{\text{kin}}$ is only a function of the kinetic reaction; this means that components are independent of the equilibrium reaction (which is actually the definition).

A.2 Speciation modelling

The transport of component species by equation (1) requires calculating the aqueous species concentration at every node of the computational domain. The concentration of aqueous species is obtained from the solution of the following eight algebraic equations (A.3 through A.10), which result from four of the equilibrium reactions (R1) to (R4) and the mineral kinetic reaction (R5):

$$\left(c_{\text{H}^+} \gamma_{\text{H}^+} c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} \right) - \left(c_{\text{CO}_2\text{aq}} \gamma_{\text{CO}_2\text{aq}} K_{\text{CO}_2\text{aq}} \right) = 0 \quad (\text{A.3})$$

$$714 \quad \left(c_{\text{H}^+} \gamma_{\text{H}^+} c_{\text{OH}^-} \gamma_{\text{OH}^-} \right) - \left(K_{\text{H}_2\text{O}} \right) = 0 \quad (\text{A.4})$$

$$715 \quad \left(c_{\text{H}^+} \gamma_{\text{H}^+} c_{\text{CO}_3^{2-}} \gamma_{\text{CO}_3^{2-}} \right) - \left(c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} K_{\text{HCO}_3^-} \right) = 0 \quad (\text{A.5})$$

$$716 \quad \left(c_{\text{NaHCO}_3\text{aq}} \gamma_{\text{NaHCO}_3\text{aq}} \right) - \left(c_{\text{Na}^+} \gamma_{\text{Na}^+} c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} K_{\text{Na}^+} \right) = 0 \quad (\text{A.6})$$

$$717 \quad u_{\text{HCO}_3} - \left(c_{\text{HCO}_3^-} - c_{\text{H}^+} + c_{\text{OH}^-} + 2c_{\text{CO}_3^{2-}} + c_{\text{NaHCO}_3\text{aq}} \right) = 0 \quad (\text{A.7})$$

$$718 \quad u_{\text{Na}} - \left(c_{\text{Na}^+} + c_{\text{NaHCO}_3\text{aq}} \right) = 0 \quad (\text{A.8})$$

$$719 \quad u_{\text{CO}_2} - \left(c_{\text{CO}_2\text{aq}} + c_{\text{H}^+} - c_{\text{OH}^-} - c_{\text{CO}_3^{2-}} \right) = 0 \quad (\text{A.9})$$

$$720 \quad c_{\text{Ca}^{2+}} = u_{\text{Ca}} \quad (\text{A.10})$$

721

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